Environmental Science & Technology
ARTICLE
pubs.acs.org/est

Quantifying In-Use PM Measurements for Heavy Duty Diesel Vehicles

Kent C. Johnson,[†,*] Thomas D. Durbin,[†] Heejung Jung,[†] David R. Cocker, III,[†] Dipak Bishnu,[‡] and Robert Giannelli[§]

[†]Center for Environmental Research and Technology (CE-CERT), College of Engineering, University of California, Riverside, California 92521, United States

[‡]California Air Resources Board (CARB), 1001 I Street, Sacramento, California 95814, United States

[§]U.S. Environmental Protection Agency (EPA), 2000 Traverwood Dr., Ann Arbor, Michigan 48105, United States

S Supporting Information

ABSTRACT: Heavy duty emissions regulations have recently expanded from the laboratory to include in-use requirements. This paradigm shift to in-use testing has forced the development of portable emissions measurement systems (PEMS) for particulate matter (PM). These PM measurements are not trivial for laboratory work, and are even more complex for in-use testing. This study evaluates five PM PEMS in comparison to UCR's mobile reference laboratory under in-use conditions. Three on-highway, heavy-duty trucks were selected to provide PM emissions levels from 0.1 to 0.0003 g/hp-h, with varying compositions of elemental carbon (EC), organic carbon (OC), and sulfate. The on-road driving courses included segments near sea level, at elevations up to 1500 m, and coastal and desert regions. The photoacoustic measurement PEMS performed best for the non-aftertreatment system (ATS)-equipped engine, where the PM was mostly EC, with a linear regression slope of 0.91 and an R^2 of 0.95. The PEMS did not perform as well for the 2007 modified ATS equipped engines. The best performing PEMS showed a slope of 0.16 for the ATS-equipped engine with predominantly sulfate emissions and 0.89 for the ATS-equipped engine with predominantly OC emissions, with the next best slope at 0.45 for the predominantly OC engine.

INTRODUCTION

Worldwide government agencies are implementing a series of regulations that will control gaseous and particulate matter (PM) emissions from diesel engines in-use and ensure that low emissions levels can be maintained throughout the course of an engine's lifetime. One of the more important regulations with respect to controlling in-use emissions is the Not-To-Exceed (NTE) regulation in the United States, which requires in-use emission testing to evaluate emissions in a defined portion of the engine operation known as the NTE control area.[1] In-use testing requires new technology that has been developed to quantify PM emissions on a mass basis under the protocols specified in the regulations. These portable emission measurement systems (PEMS) for PM are specifically designed to measure PM mass during short NTE events.

There have been many comparisons of real-time PM mass measurement instruments with laboratory-based gravimetric reference methods[28]. Although these studies have shown reasonably good correlations between PM gravimetric mass and real-time PM mass, their widespread use, covering the range of emission levels for diesel PM (engine-out and trap-equipped) over different operating conditions, is not well understood. Some studies have also shown that the measurement principle assumptions used by many instruments do not hold for all PM combustion sources, regardless of whether the principle is absorbed energy, electrical mobility, inertial, or light scattering properties.[2] Others in the scientific community have suggested that adsorption artifacts for the gravimetric filter reference method could cause correlation differences.[5]

Two new PM instruments were commercialized in 2008 because there was a lack of available technologies to correlate reliably with the gravimetric method over short periods of time. One technology uses a quartz crystal microbalance (QCM) to directly measure the weight gain of deposited PM mass.[9,10] The other uses a combination of a gravimetric reference filter and a real-time electrical charge carried by the particles.[11] These new PM PEMS are commercially available, but neither has been fully tested nor evaluated by independent researchers. As of 2009, the U.S. Environmental Protection Agency had shown data that suggested a QCM version, with a prototype single crystal head, had excellent correlation with gravimetric mass under laboratory conditions.[12] The other PM PEMS had only been evaluated by manufacturer-sponsored

Received: December 10, 2010
Accepted: June 9, 2011
Revised: June 7, 2011
Published: June 09, 2011

Table 1. Test Vehicles Used During the In-Use Evaluation

vehicle	engine	ATS	vehicle mileage	PM emissions controls	PM range[a] g/hp-h
2001 Freightliner	2000 Caterpillar C15	no	18 000	(1) none	0.02–0.1
2008 Prostar	2007 Cummins ISX450	yes	17 500	(1) regenerations[b] (2) ECM recalibration	0.001–0.01
2008 Volvo	2007 Volvo D13-F485	yes	500	(1) regenerations (2) ECM recalibration (3) ATS bypass	0.001–0.04

[a] PM range is the range of PM emissions measured during the testing program. [b] Regeneration is a process where fuel is injected in the exhaust before the DPF in order to reduce the PM loading on the DPF.

testing that showed agreement on laboratory transient tests of better than 10%.[11]

For this study, several PM PEMS were directly compared with the University of California, Riverside's (UCR) Mobile Emissions Laboratory (MEL) over a series of different on-road driving conditions. The MEL is unique in that it contains a full 1065-compliant constant volume sampling (CVS) system with gravimetric PM measurements, while being fully operational under on-road driving conditions. Measurements were made from two modified aftertreatment system (ATS)-equipped, Class 8 heavy-heavy duty trucks and one non-ATS–equipped, Class 8 heavy-heavy duty truck. The ATS systems included an original equipment manufacturer (OEM) diesel oxidation catalyst (DOC) and a diesel particulate filter (PDF) with an exhaust fuel injection regeneration management system.

This study represents the first in-use evaluation of the new PM PEMS and other PM instruments compared to a mobile reference laboratory meeting regulatory requirements. The work is also unique that it includes a wide range of PM emission levels, compositions, and particle size distributions. The on-road driving courses included segments near sea level, in coastal regions, in desert regions, and on longer uphill inclines. The results presented represent a robust in-use evaluation of the PM PEMS systems as they compare to the traditional reference system.

EXPERIMENTAL SECTION

Test Vehicles. Three heavy–heavy duty diesel vehicles were selected for this in-use PM PEMS evaluation. The vehicles selected comprised one non-ATS diesel engine and two ATS-equipped diesel engines, as listed in Table 1. The non-ATS engine was a 2000 Caterpillar engine and the two ATS-equipped engines were a 2007 Cummins and a 2007 Volvo engine. The MEL trailer itself provided the load for all the on-road testing. The gross vehicle weight of the tractors and trailer was about 65 000 lbs for all the in-use testing performed. All the engines had similar peak torque and peak power and ranged from 1650 to 1690 ft-lb and 450 to 485 hp, respectively. During all testing, commercially available CARB ultra low sulfur diesel (ULSD) fuel with a sulfur level of less than 15 ppm was used.

The non-ATS-equipped vehicle was selected to provide PM emission levels up to 0.1 g/hp-h, whereas the ATS-equipped vehicles were selected to provide emissions near 0.01 g/hp-h. Typical PM emissions from a properly functioning DPF are near 0.001 g/hp-h. The PM emission levels for the ATS-equipped engines were manipulated in order to evaluate the PM PEMS around the 0.01 g/hp-h standard. Three approaches were used to manipulate the PM emission levels for the ATS-equipped engines: electronic control module (ECM) recalibrations, DPF-controlled regenerations, and an ATS bypass, as listed in Table 1. The ATS bypass takes a portion of the engine out exhaust and routes it around the DPF. The use of an ATS bypass simulates higher PM emissions that may be more representative of levels that might be seen for a malfunctioning DPF. For more details on the approach used for regenerations, ATS bypass, and ECM recalibration, see.[13] In general, the emission control modifications varied the brake specific PM (bsPM) levels and provided a range of PM for the ATS-equipped vehicles that varied from 0.0003 to 0.04 g/hp-h, as listed in Table 1

PEMS Description. A total of five PEMS systems were tested as part of this in-use PM measurement evaluation. These five PEMS represent different levels and types of technology, as listed in Table 2. The PEMS are labeled by number and operational principles. Both PEMS1, which uses diffusion charging along with a gravimetric filter (DC+F), and PEMS2(QCM) are complete systems with the self-contained ability to measure PM mass, exhaust flow rate, regulated gaseous emissions, and the engine parameters needed to calculate the applicable criteria for bsPM during short 30 s NTE events. PEMS3, which uses a photoacoustic (PA) measurement principle, was designed to sample from the raw exhaust, but did not have an integrated system measuring for exhaust flow and integrated ECM parameters. PEMS3(PA) was used in conjunction with PEMS1 or 2 to get in-use bsPM. PEMS4 uses electrical mobility and aerodynamic impaction (EM+A) measurement principle and PEMS5 uses light scattering (LS) measurement principle. PEMS4(EM+A) and PEMS5(LS) were setup and installed in the MEL laboratory and measured from the diluted exhaust rather than the raw exhaust.

The PEMS that sampled from the raw exhaust utilized heated sample lines and close coupled dilution following the requirements of 40 CFR Part 1065. For PEMS1(DC+F) and PEMS2(QCM), the dilution was proportional to the exhaust flow. Proportionality is required because these PEMS are depositing PM mass on surfaces that must be flow-weighted in order to measure the PM mass properly. PEMS3(PA) system makes continuous measurements with a constant sample flow, which was not proportional to the exhaust flow.

PEMS1(DC+F) is Horiba's Transient Particulate Matter system (TRPM). The principle of operation is based on a combination of direct mass measurements using a gravimetric filter and diffusion charging from an integrated electrical aerosol detector (EAD).[11] PEMS2(QCM) is Sensor Inc.'s Portable Particulate Mass Device (PPMD). The PM mass measurement is based on QCM technology that employs piezoelectric crystals, where aerosol particles are deposited on a crystal surface after being charged in a high concentration of unipolar ions[9,14,15]. The charged particles enter an electric field and are attracted to the

Table 2. Test Matrix for Previous and Current PM PEMS In-Use Evaluations

ID	alt ID	measurement principle	mount location	dilution ratio[a]	proportional sampling	sample location
PEMS1	DC+F	**d**iffusion **c**harging + **g**ravimetric **f**ilter	tractor frame	6	yes	raw exhaust
PEMS2	QCM	**q**uartz **c**rystal **m**icrobalance	tractor frame	6−50	yes	raw exhaust
PEMS3	PA	**p**hoto-**a**coustic	tractor frame	2−4	no	raw exhaust
PEMS4	EM+A	**e**lectrical **m**obility + **a**erodynamic impaction	MEL	6−100	no	CVS and secondary dilution
PEMS5	LS	90°**l**ight **s**cattering	MEL	6	no	CVS

[a] Dilution ratio reported at maximum exhaust flow of 1000 scfm.

crystal surface where they are deposited. The oscillation frequency of the crystal decreases with increasing mass load. By detecting the frequency change of the crystal, the mass deposited can be determined. See Supporting Information A for more information on PEMS descriptions, operation, and special issues related to the PEMS, such as crystal greasing.

PEMS3(PA) system is AVL's micro soot sensor (MSS) model 483. This PEMS uses the PA measurement principle, which provides a PM measurement that more directly corresponds to soot or EC as opposed to PM mass (3,16,17, 18). PEMS4(EM+A) is Dekati's Mass Monitor (DMM) 230. This PEMS measures PM mass concentrations through a combination of a constant voltage, sub 30 nm, electrical mobility detector and aerodynamic inertial impaction. There are six stages of aerodynamic impaction from 30 to 532 nm used to estimate the mass concentration.[3,5] PEMS5(LS) is TSI's DustTrak 8520. PEMS5(LS) was calibrated to diesel exhaust using measurements by the MEL back in 2005, and it has been using this same calibration ever since.[3]

PEMS Operation and Installation. PEMS1(DC+F), PEMS2(QCM), and PEMS3(PA) were mounted on a frame attached to the tractor for all the in-use testing, while PEMS4(EM+A) and PEMS5(LS) were mounted within the MEL. The operation for all instruments was performed according to the manufacturer's specifications. The operation of PEMS2(QCM) and PEMS3(PA) differed somewhat from vehicle-to-vehicle based on the different testing conditions for each vehicle, as described in more detail in the Supporting Information A. PEMS4(EM+A) and PEMS5(LS) sampled from the MEL's CVS.

MEL Operation. The MEL's primary tunnel flow rate was set to 2700 standard cubic feet per minute (scfm) and the secondary tunnel was set to provide a secondary dilution of 2.27:1. The actual dilution ratio varied from a maximum of 17:1 to a minimum of 7:1, with an average DR of 11 ± 2:1. These dilution ratios created a CVS sample temperature that averaged 80 °C with a single standard deviation of 20 °C throughout the test program.

MEL PM Measurements. The reference PM mass was collected on Pall Teflo 2 μm pore filters. The filters were sampled following 40 CFR Part 1065, with the exception that the Caterpillar testing was performed with face velocities of 50 cm/s instead of the recommended 100 cm/s. The MEL was upgraded for the 2007 Cummins and Volvo tests so that the required 100 cm/s face velocity could be utilized.

PM composition, size distribution and particle number were also measured during this study. EC and OC were measured from samples collected on Tissuquartz filters. The EC/OC analysis was performed with a Sunset Laboratory Thermal/Optical Carbon Aerosol Analyzer according to the NIOSH 5040 reference method. Sulfur was analyzed from the same Teflo filters used for the gravimetric measurements. The sulfur analyses were performed using a Dionex DX-1000 ion chromatograph to determine the mass of sulfate ions on the filters. Sulfate in PM was assumed to be in the hydrated form, $H_2SO_46.5(H_2O)$, hence a factor of 2.33 was applied to the mass of sulfate ions to determine its total contribution to the PM mass presented in the Results section. Particle size distributions were analyzed with a fast-scanning mobility particle sizer (fSMPS) that has a scanning time of a few seconds compared to the 60−90 s for a more traditional SMPS.[19] Particle number concentrations were characterized with a TSI condensation particle counter (CPC) 3760 with a cut point of 11 nm.

Reference Accuracy. The MEL was cross compared with an engine dynamometer test cell CVS at the Southwest Research Institute (SwRI) in San Antonio TX. The measurements were done at an emission level of 0.025 g/hp-h for PM. The MEL was, on average, lower than SwRI by about 6% on a simulated NTE transient cycle. The 6% difference is well within the measurement variability of other round robin studies[23] and suggests the MEL is a reasonable reference tool for comparing PM PEMS under in-use conditions and quantifying the associated PEMS uncertainties. Some of the conditions for the Cummins and Volvo tests were at much lower PM concentrations than those from the cross correlation, where the reference filter weights have more uncertainty. See Supporting Information B for more information on the MEL reference method uncertainty at different PM measurement levels.

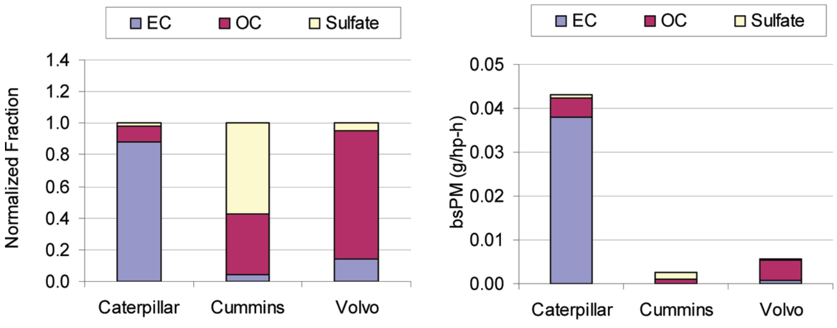
Test Routes. The PEMS were tested over routes similar to those used during a previous gaseous PEMS evaluation program,[20] with some that were new for this test program. The routes were designed such that the elevation varied from sea level to 1500 m, humidity varied from 10 to 80%, ambient temperature varied from 10 to 43 °C, and several large power lines were passed.

RESULTS

The experimental results and cross comparisons between the different PM PEMS and the MEL are presented in this section for the 2000 Caterpillar, 2007 Cummins, and 2007 Volvo engines.

PM Analysis Basis. The PM analysis was done on a brake specific basis for the on-highway conditions in a work zone defined by NTE regulations, as mentioned earlier. The NTE work zone excludes operation when the engine is at low loads, a condition where the brake specific emissions are exaggerated by low values of the work term. For more information on the conditions for each event, see Supporting Information C. Filter weights for the non-ATS engine were 129 μg on average. Filter weights were lower for the ATS-equipped engines, ranging from a few μg to more than 200 μg with an average of 50 μg. The presented results are not corrected for tunnel blanks, which were just under 5 μg. For more information on tunnel blanks and the reference system uncertainty, see Supporting Information B.

PM Composition. Figure 1(a) shows the normalized PM composition and Figure 1(b) shows the averaged bsPM emissions by composition for all three test engines summarized in bar



(a) (b)

Figure 1. Normalized PM fractions (a) and bsPM fractions (b) for All Test Engines.

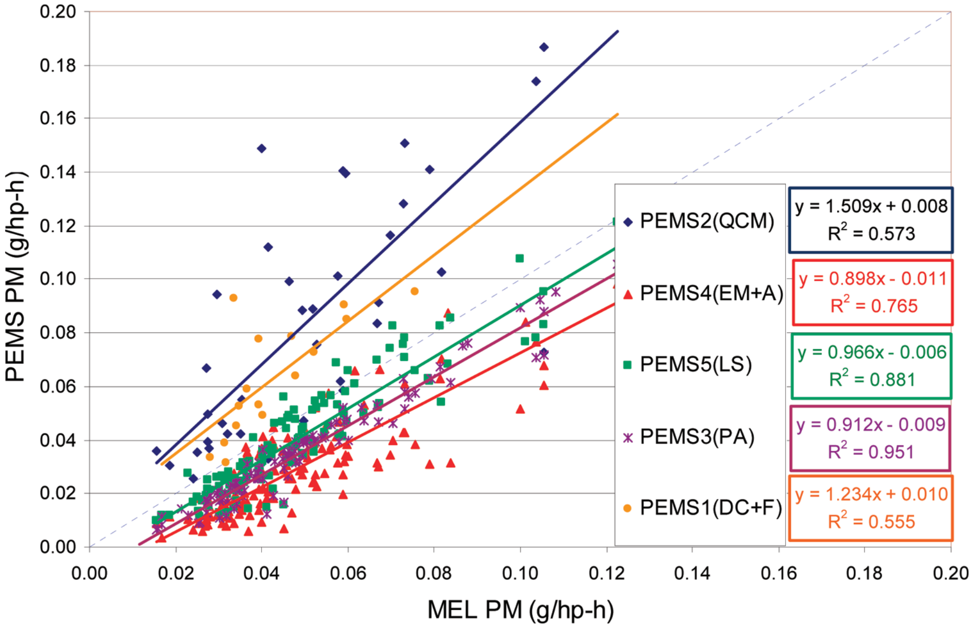


Figure 2. bsPM Correlation Between the MEL and PEMS (Caterpillar).

charts. The Caterpillar EC and OC data presented is based on a previous study,[21,22] where selected forced events were analyzed for sulfate mass. The mass balance between the composition data and the gravimetric mass was found to be in good agreement, see Supporting Information D for more information. In general, the figures show that the three test engines differed not only by emission levels, but also in PM composition.

Overall, the Caterpillar PM (from a 2000 non-ATS engine) was mostly EC with small amounts of OC and trace amounts of sulfate mass, see Figure 1(a). All the Caterpillar sulfate measurements were at the detection limits of the instrument. The Cummins engine showed a majority fraction of the PM from sulfate with OC representing most of the remaining mass. The OC mass, though, was just above the detection limits of the method. The Volvo samples were mostly composed of OC, with small amounts of EC and very little sulfate. The Volvo sulfate levels were higher than the Caterpillar levels, but were still close to, if not at, the detection levels of the instrument. See Supporting Information D for more information on the detection limits for EC, OC, and sulfate analysis. The lower sulfate PM for the Volvo compared to the Cummins could be due to differences in ATS sulfur exposures, as seen by the differences in the accumulated miles for the vehicles of 500 and 17,500 mi, respectively. The Volvo PM also had more OC and EC than the Cummins, which could be directly related to the bypass installed around the Volvo aftertreatment device.

Particle Number Count and Size Distribution. Particle number (CPC 3760) and size distributions (fSMPS) were measured for both the Cummins and Volvo tests. The Cummins tests showed, on average, about five times more particles for the same given mass compared to the Volvo tests.[13] The size distributions for the Cummins showed a peak diameter between 10 and 30 nm, with relatively few particles above 40 nm, while the Volvo size distributions showed a much larger peak diameter of around 60−100 nm.[13] Previous measurements for the Caterpillar vehicle show that the Caterpillar particle sizes were slightly larger than those for the Volvo, with a particle number average diameter of around 80 to 120 nm for similar duty cycles.[19] See Supporting Information E for more information on particle size distributions.

PM Mass Results. Figure 2−4 show the PEMS bsPM correlation to the MEL bsPM for the Caterpillar, Cummins

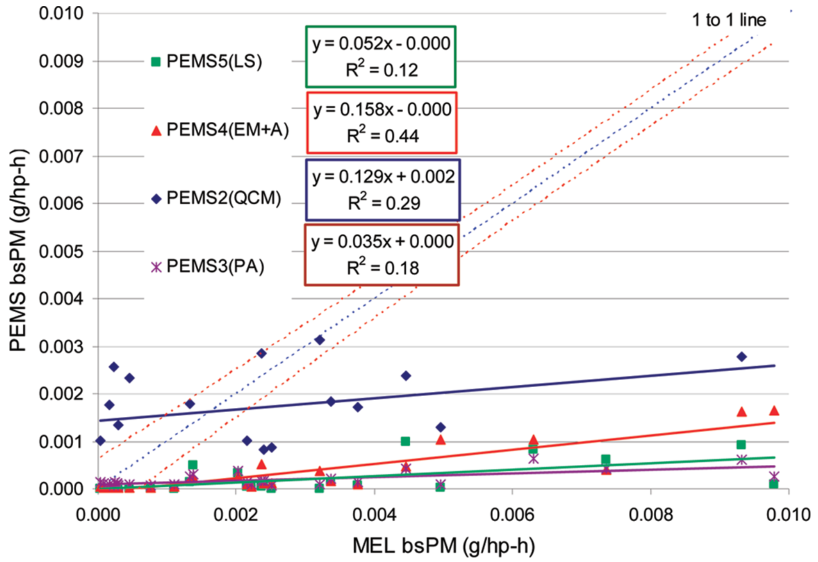


Figure 3. bsPM Correlation Between the MEL and PEMS (Cummins).

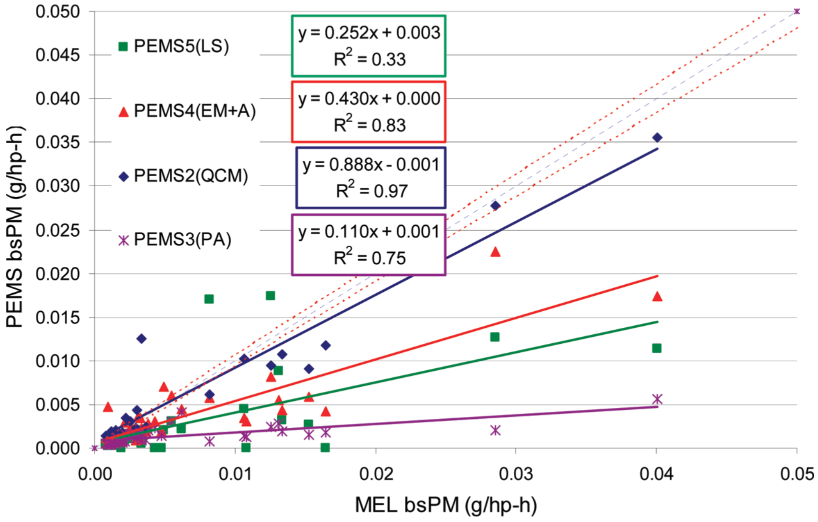


Figure 4. bs PM Correlation Between the MEL and PEMS (Volvo).

and Volvo, respectively. The lightly dashed blue line in each of the figures represents a one-to-one line for perspective on the PEMS biases relative to the MEL. The ATS-equipped engines provided low bsPM emission levels, where filter weights were significantly reduced compared to the Caterpillar testing. An error weighted, least squared analysis approach was used for the correlation in Figure 3 and 4. Also added to Figures 3 and 4 is a filter weight uncertainty line denoted by the faint red dotted line. The filter weight uncertainty is defined as ($3 \times 2.5\ \mu$g/net filter weight), where 2.5 μg is the typical uncertainty for replicate weights of a reference filter. The reference uncertainty can be attributed to a number of possible factors that can either increase or decrease the filter mass. Thus, the uncertainty may not actually be distributed evenly to the plus or minus side. A complete discussion of the reference uncertainty is provided in.[13,24]

PEMS Discussions. In general, PEMS3(PA), PEMS4(EM+A), and PEMS5(LS) showed a good correlation with a slightly low bias for the Caterpillar tests, and PEMS1(DC+F) and PEMS2(QCM) showed a relatively poor correlation and a high bias, as seen in Figure 2. The PEMS1(DC+F) correlation represents only the last day of testing where the PEMS was operating without technical issues. All the PEMS showed a poor correlation for the Cummins vehicle, with the exception that PEMS1(DC+F) was not tested for that vehicle. For the Cummins vehicle, PEMS4(EM+A) showed the best correlation, but was still only measuring about 16% of the reference mass. PEMS2(QCM) showed the best correlation for the Volvo tests, where it measured 89% of the reference mass. PEMS4(EM+A) was the next best for the Volvo tests, but it measured less than 50% of the reference mass.

PEMS1(DC+F). PEMS1(DC+F) was only tested for the Caterpillar equipped vehicle. This instrument had technical difficulties during its first three days of testing, so only the last day was considered valid. The results for the Caterpillar tests showed a correlation with an R^2 of 0.55 and a slope of 1.23. This suggests the PEMS1(DC+F) system overestimated the PM mass by about 23%, but with a marginal correlation. This PEMS data are considered as the "best available" measurements at the time of this research. It is expected that the results for the PEMS will improve given more development time.

PEMS2(QCM). The PEMS2(QCM) showed a poor correlation for the Caterpillar testing that may be related to a high concentration of dry soot particles. The Caterpillar tests showed relatively high PM emissions, composed of predominantly EC. EC dominated PM is known to be dry or difficult to deposit on hard surfaces, like quartz. The crystals showed a decaying PM response at 0.2 μg crystal loadings, which suggests the surface is overloaded or not depositing as efficiently as with a clean surface. In order to prevent this so-called overloading condition, the dilution ratio was increased from 6:1 to about 50:1 and the sample flow was dropped from 0.4 to 0.25. These changes in operating parameters are typical for this instrument, and would likely be needed for other vehicles with PM characteristics similar to those of the Caterpillar.

The PEMS2(QCM) showed a poor correlation for the Cummins tests, as shown in Figure 3, where there was a large sulfate contribution to the PM composition. It is expected that the gravimetric sulfate mass will have a different water hydration level than the PEMS2(QCM) mass due to different PM conditioning. The PEMS2(QCM) conditioning is shorter (minutes versus hours), at higher temperatures (47 °C versus 22 °C), and at variable humidity compared to the constant 45% humidity in the gravimetric weighing chamber. The different conditioning environments could cause a bias, but the bias should be bound by the factor of 2.33 for hydrated sulfate (as discussed earlier). Thus, the contribution of water hydration alone cannot explain the poor correlation. This suggests that the PEMS2(QCM) system may have a measurement issue with PM that is dominated by small, nucleation mode, sulfate particles. The large sulfate PM contribution and small particle number averaged diameters of 10−30 nm for the Cummins tests suggest the particles contributing to the PM mass are formed from the conversion of SO_2 to SO_3 over the catalytic surfaces in the ATS during regeneration conditions. These nanoparticles can form via homogeneous nucleation during the dilution process, and grow in size. Thus, it is possible differences between full dilution and proportional dilution may have caused some of the particle mass differences between the PEMS2(QCM) and the reference. Another reason for the low PEMS2(QCM) response could be due to lower charging efficiencies for nucleation mode type particles.[25]

The best correlation for PEMS2(QCM) was for the Volvo tests, where the R^2 was 0.97 with a slope of 0.89. The slope was still below one, and thus the bsPM is still underestimated by about 11% compared to the reference. The good correlation suggests that PEMS2(QCM) does not have any significant measurement difficulties for OC dominated PM with a peak diameter from 60−100 nm.

PEMS3(PA). The slightly low bias for the Caterpillar PEMS3(PA) results is consistent with this instrument only measuring the EC portion of the PM mass. The Caterpillar composition was 90% EC with the remainder being OC and sulfate. The 90% EC figure is consistent with the 10% low bias for PEMS3(PA) for the Caterpillar. These results agree with those from a previous study conducted under more controlled conditions.[3] During the Cummins and Volvo testing, though, PEMS3(PA) only measured 4% and 11% of the mass of the reference, respectively. Properly functioning DPF's produce almost no soot, so most of the PM is from the dilution process. Hence, the observation of a low PEMS3(PA) mass relative to the reference method can be attributed to the other components and formation processes, as expected.[16,18] Bypassing the DPF typically provides elevated PM soot concentrations. Thus, the increase in PEMS3(PA) response between the Cummins and the Volvo results are most likely a result of the slight increase in EC due to the ATS bypass modifications, as shown in Figure 1. In general, the PEMS3(PA) measurement system was only effective for the high soot case (Caterpillar engine), and not the high sulfate (Cummins engine), and high OC (Volvo engine) cases, as expected based on its measurement principle. The PEMS3(PA) manufacturer recently released a new version of this PEMS which includes a gravimetric filter similar to PEMS1(DC+F). It is expected that the PEMS3(PA) with the gravimetric filter may show better performance for measuring PM with a high OC or sulfate contribution.

PEMS4(EM+A). The good correlation for the Caterpillar testing agrees with another PEMS4(EM+A) evaluation,[5] where PEMS4(EM+A) was biased slightly low and captured about 90% of the reference mass. For the ATS-equipped engines, however, PEMS4(EM+A) underreported PM mass, capturing only 16% of the reference mass for the Cummins, and a somewhat higher 43% of the reference mass for the Volvo. During the Cummins testing, the particles were smaller than the lowest 30 nm impactor stage. For the Volvo testing, the particle size was larger, but not as large as particles from the Caterpillar testing. The improvement in mass response from the Cummins to the Volvo to the Caterpillar tests, where particles increased in size between each vehicle tested, suggests PEMS4(EM+A) may be sensitive to variations in particle size.

PEMS5(LS). The PEMS5(LS) correlated well for the Caterpillar tests and showed the slope closest to unity (i.e., slope = 0.97) compared to the other PEMS. The good correlation was expected since PEMS5(LS) was calibrated previously with the MEL as discussed earlier. The PEMS5(LS) Cummins correlation was poor, and it measured only 5% of the reference mass. The mass recovery improved from the Cummins to the Volvo, with 25% of the reference mass being measured for the Volvo tests. The differences between the mass measurements for the Cummins and Volvo could be related to the significant role particle size plays in light scattering theory[25] and the fact that particle size peak changed from 10 to 30 nm to 60−100 nm from the Cummins to the Volvo.

This research identified a number of key issues with in-use testing of PM. Recently released PM PEMS vary significantly in their correlation to the gravimetric reference method. Generally, the correlations were relatively poor with overreporting for pre-2007 technology and underreporting for ATS-equipped engines. The underreporting for the ATS-equipped Cummins can be attributed to the high sulfate PM from regenerations, while the underreporting for the ATS-equipped Volvo can be attributed to the high OC PM resulting from the ATS bypass.

Overall, it appears that PM PEMS at the development level of those tested in this study are not sufficient to characterize the full range of PM levels and compositions that might be found for malfunctioning ATS-equipped engines. The biases, both negative and positive, also suggest that PM emission factors for in-use emissions will inherently contain errors if they are based solely or heavily on in-use PM PEMS measurements. This suggests that PM measurements from a broader range of engine and chassis dynamometer laboratory measurements are still needed for the development of PM emissions inventories.

The development of new and improved in-use PM measurement tools are critical, and expected to continue. Recently, the PEMS3(PA) system was improved to provide an integrated gravimetric filter to better measure PM with low EC and high OC and sulfate. While this new PM PEMS shows promise and is currently being evaluated, it is unknown how it will work for the variety of possible PM levels, compositions, and size distributions that could be found for properly and improperly functioning ATSs. In general this study suggests that the inclusion of gravimetric filter measurements in conjunction with real-time, in-use PEMS testing might help to assess PM PEMS accuracy and better characterize vehicle PM emissions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. PM Composition, sampled events, particle size distribution, and PEMS installation and description. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kjohnson@cert.ucr.edu.

■ ACKNOWLEDGMENT

The California Air Resources Board (CARB), U.S. Environmental Protection Agency, and Engine Manufacturer's Association (EMA) funded this work. The authors acknowledge the support of the Measurement Allowance Steering Committee (MASC) for assistance in developing and carrying out this program. We acknowledge Sensors Inc., Horiba, and AVL for providing the PM PEMS as an in-kind contribution for a part of the program. We acknowledge Caterpillar, PACCAR, and International for the use of their PM PEMS equipment. We also acknowledge Caterpillar, Volvo and Cummins for their onsite engineering assistance. Lastly, we acknowledge Mr. Donald Pacocha and Mr. Joe Valdez, University of California at Riverside, for their contribution in setting up and executing this field project, the data collection and quality control.

■ REFERENCES

(1) 40CFR 86.1370-2007, Not-To-Exceed Test Procedures, 65 Federal Register 59958, Oct. 6, 2000

(2) Bergmann, M., Scheer, V., Vogt, R., Benter, T. *Instrumentation for Vehicle Exhaust Measurements* SAE 2007-24-0116 SAE International: Warrendale, PA, 2007.

(3) Durbin, T. D., Johnson, K. C., Cocker, D. R. Miller, J. W., (**2007**) Evaluation and comparison of portable emission measurement systems and federal reference methods for emissions from a back-up generator and a diesel truck operated on a chassis dynamometer, *Environ. Sci. Technol.* **2007**, 41, 6199–6204.

(4) Kittelson, D. B., Hands, T., Nickolaus, C. *Mass Correlation of Engine Emissions with Spectrial Instruments*, JSAE Paper 20045462; Society of Automotive Engineers Japan: Tokyo, 2004.

(5) Lehmann, U.; Niemela, V.; Morh, M. New methods for time resolved diesel engine exhaust particle mass measurements. *Environ. Sci. Technol.* **2004**, *38*, 5704–5711.

(6) Maricq M. M., Xu N., Chase R. E., (**2006**) Measuring particulate mass emissions with electrical low pressure impactor, *Aerosol Sci. Technol.* (2006) Vol *40*: 68-79.

(7) Podsiadlik, D. H., Chase, R. E., Lewis, D., Spears, M. *Phase-Based Teom Measurements Compared With Traditional Filters for Diesel PM*, SAE 2003-01-0783; SAE International: Warrendale, PA, March, 2003.

(8) Witze, P. O., Maricq, M. M., Chase, R. E., Podsiadlik, D. H., Xu, N. *Time-Resolved Measurements of Exhaust PM for FTP-75: Comparison of LII, ELPI, and TEOM Techniques*, SAE 2004-01-0964; SAE International: Warrendale, PA, 2004.

(9) Booker, D. R. Giannelli, R. A., Hu, J. *Road Test of an on-Board Particulate Matter Mass Measurement System*, SAE 2007-01-1116; SAE International: Warrendale, PA, 2007.

(10) Lundgren, D. A., Carter, L. D., Daley, P. S. Aerosol mass measurement using piezoelectric crystal sensors in fine particles, aerosol generation. In *Measurement Sampling, and Analysis*; B. Y. H., Liu, Ed.; Academic Press: New York, 1976.

(11) Wei, Q., Akard, M., Porter, S. Nakamura, H. *The Development of an On-Board Instrument for On-Road Diesel Particulate Measurement*, SAE 2008-36-0273; SAE International: Warrendale, Pa, 2008.

(12) Spears, M. W. Portable Emission Measurement Strategy — Update on Recent Activities. In *Proceedings of the 12th CRC On-Road Vehicle Emissions Workshop*; San Diego, CA, April 2002.

(13) Durbin, T. D., Jung, H., Cocker, D. R., Johnson, K. C. PM PEM's On-Road Investigation — With and Without DPF Equipped Engines, Final Report for the California to Engine Manufacturing Association, July 2009. http://eprints.cert.ucr.edu/506/ (accessed April 2011).

(14) Sauerbrey, G., Z. Verwendung von Schingquarzen sur Wagung Junner Schichten und zur Microwagung. *Z. Phys.*, **1959**, *155*, 206—222, .

(15) Ward, M., D. Buttry D.,A. In situ interfacial mass detection with piezoelectric transducers. *Science* **1990**, *249*, 1000—1007.

(16) Bell, A.,G. *Phil. Mag. J. Sci.* **1881**, *XI*, 510–528.

(17) Frans, J.,M., Harren, Gina, Cotti, Jos Oomens, Sacco te Lintel Hekkert Photoacoustic spectroscopy in trace gas monitoring. In *Encyclopedia of Analytical Chemistry*; Meyers, R.A., Ed.; John Wiley & Sons Ltd: Chichester, UK, 2000; pp 2203—2226.

(18) Schindler, W., Haisch, C., Beck, A. H., Niessner, R., Jacob, E., Rothe, D. *A Photoacoustic Sensor System for Time Resolved Quantification of Diesel Soot Emissions*, SAE 2004-10-0968; SAE International: Warrendale, PA, 2004

(19) Shah, S., D., Cocker, D. A fast scanning mobility particle spectrometer for monitoring transient particle size distributions. *J. Aerosol Sci.* **2005**, *39*, 519—526, http://eprints.cert.ucr.edu/261/.

(20) Johnson K. C., Durbin T. D., Cocker III D. R., Miller W. J., Bishnu D. K., Maldonado H. Moynahan N, Ensfield C., Laroo C. A. On-road comparison of a portable emission measurement system with a mobile reference laboratory for a heavy duty diesel vehicle. *Atmos. Environ.*, **2009**, http://eprints.cert.ucr.edu/338/.

(21) Cocker, D. R.; Shah, S. D.; Johnson, K. C.; Miller, J. W.; Norbeck, J. M. Development and application of a mobile laboratory for measuring emissions from diesel engines. 1. Regulated gaseous emissions. *Environ. Sci. Technol.* **2004a**, *38*, 2182–2189.

(22) Cocker, D. R.; Shah, S. D.; Johnson, K. C.; Zhu, X.; Miller, J. W.; Norbeck, J. M. Development and application of a mobile laboratory for measuring emissions from diesel engines. 2. Sampling and toxics and particulate matter. *Environ. Sci. Technol.* **2004b**, *38*, 6809–6816.

(23) CRC E-55, Traver, M. L. *Interlaboratory Crosscheck of Heavy Duty Vehicles Chassis Dynamometers*, CRC Project No. E-551, May 2002.

(24) Durbin, T. D., Jung, H., Cocker, D. R., Johnson, K. C. PM PEM's pre-measurement allowance — on-road evaluation and investigation. In *Final Report for the Heavy Duty In-Use Testing Steering Committee* January 2009a; http://eprints.cert.ucr.edu/507/ (accessed April 2011).

(25) Hind, C. W. *Aerosol Technology: Properties, Behaviors, and Measurements of Airborne Particles*, 2nd ed.; Wiley-Interscience Publishing: New York, 1989.